

(312) 906-7769

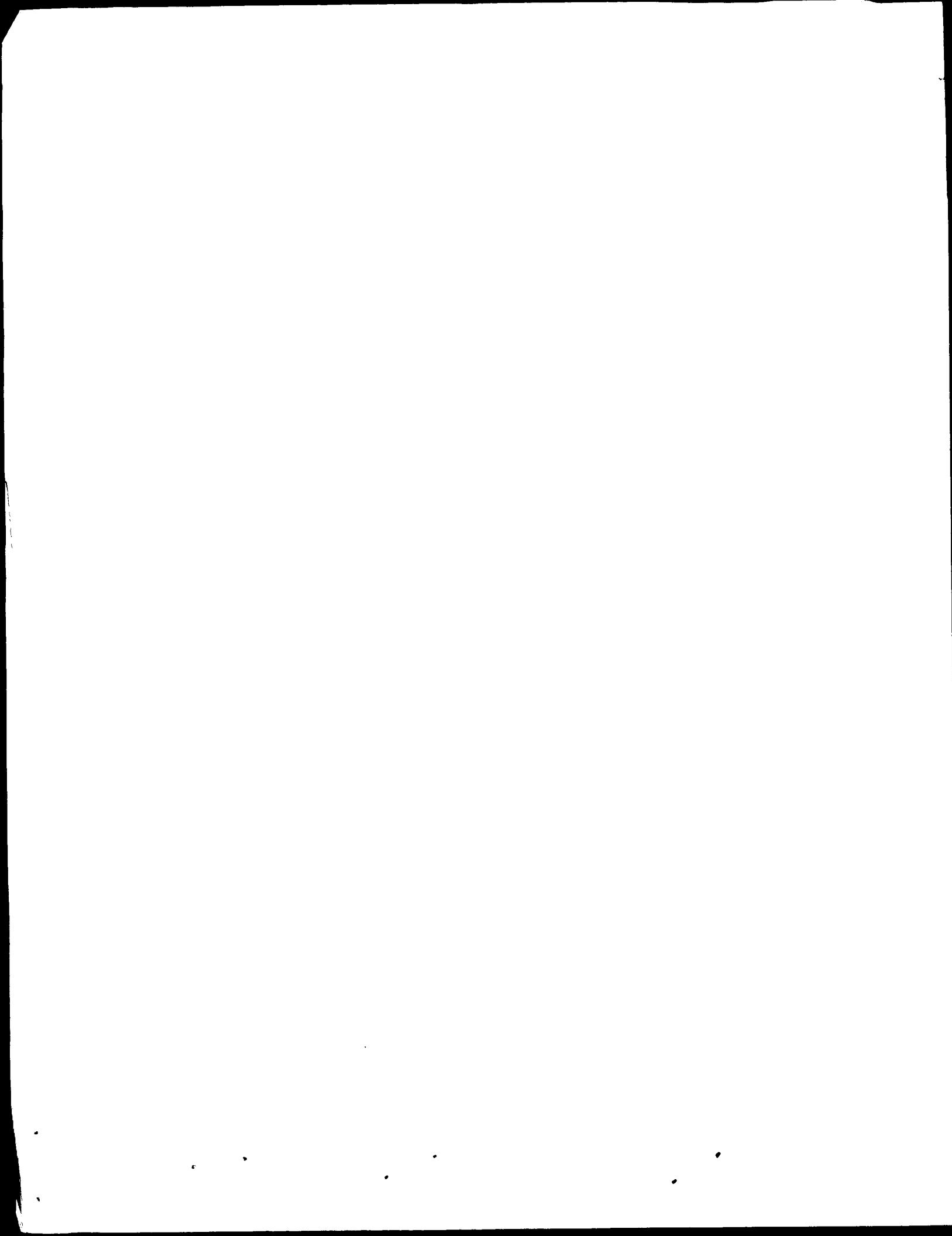
Dobbs Ferry, N.Y. 10522

7 Lvingstone Avenue

Intellectual Property Department

Akzo Nobel Inc.

Reg. No. 28,100



DEN HAG, DEN
THE HAGUE,
LA HAYE, ILE

08/02/02

R C van Dijk


 P.o.
 Le Président de l'Office européen des brevets
 For the President of the European Patent Office
 im Auftrag
 Der Präsident des Europäischen Patentamts;

01200831.4

Patentanmeldung Nr. Patent application No. Demande de brevet n°

Die angehefteten Unterlagen sind die originalen Ausgaben der eingereichten europäischen Patentanmeldung. Sie enthalten alle erforderlichen Angaben und sind in der Reihenfolge, in der sie dem Nachlass beigegeben wurden, aufgestellt. Die entsprechenden Kopien sind als Nachdrucke der originalen Ausgaben zu verstehen.

Bescheinigung Certificate Attestation



Europäisches Patentamt
European Patent Office
Office européen des brevets



1960-1961 - 1962-1963 - 1963-1964 - 1964-1965 - 1965-1966 - 1966-1967

1967-1968 - 1968-1969 - 1969-1970 - 1970-1971 - 1971-1972 - 1972-1973

1973-1974 - 1974-1975 - 1975-1976 - 1976-1977 - 1977-1978 - 1978-1979

1979-1980 - 1980-1981 - 1981-1982 - 1982-1983 - 1983-1984 - 1984-1985

1985-1986 - 1986-1987 - 1987-1988 - 1988-1989 - 1989-1990 - 1990-1991

1991-1992 - 1992-1993 - 1993-1994 - 1994-1995 - 1995-1996 - 1996-1997

1997-1998 - 1998-1999 - 1999-2000 - 2000-2001 - 2001-2002 - 2002-2003

2003-2004 - 2004-2005 - 2005-2006 - 2006-2007 - 2007-2008 - 2008-2009

2009-2010 - 2010-2011 - 2011-2012 - 2012-2013 - 2013-2014 - 2014-2015

2015-2016 - 2016-2017 - 2017-2018 - 2018-2019 - 2019-2020 - 2020-2021

2021-2022 - 2022-2023 - 2023-2024 - 2024-2025 - 2025-2026 - 2026-2027

2027-2028 - 2028-2029 - 2029-2030 - 2030-2031 - 2031-2032 - 2032-2033

2033-2034 - 2034-2035 - 2035-2036 - 2036-2037 - 2037-2038 - 2038-2039

2039-2040 - 2040-2041 - 2041-2042 - 2042-2043 - 2043-2044 - 2044-2045

2045-2046 - 2046-2047 - 2047-2048 - 2048-2049 - 2049-2050 - 2050-2051

2051-2052 - 2052-2053 - 2053-2054 - 2054-2055 - 2055-2056 - 2056-2057

2057-2058 - 2058-2059 - 2059-2060 - 2060-2061 - 2061-2062 - 2062-2063

2063-2064 - 2064-2065 - 2065-2066 - 2066-2067 - 2067-2068 - 2068-2069

2069-2070 - 2070-2071 - 2071-2072 - 2072-2073 - 2073-2074 - 2074-2075

2075-2076 - 2076-2077 - 2077-2078 - 2078-2079 - 2079-2080 - 2080-2081

2081-2082 - 2082-2083 - 2083-2084 - 2084-2085 - 2085-2086 - 2086-2087

2087-2088 - 2088-2089 - 2089-2090 - 2090-2091 - 2091-2092 - 2092-2093

2093-2094 - 2094-2095 - 2095-2096 - 2096-2097 - 2097-2098 - 2098-2099

2099-20100 - 20100-20101 - 20101-20102 - 20102-20103 - 20103-20104 - 20104-20105

20105-20106 - 20106-20107 - 20107-20108 - 20108-20109 - 20109-20110 - 20110-20111

20111-20112 - 20112-20113 - 20113-20114 - 20114-20115 - 20115-20116 - 20116-20117

20117-20118 - 20118-20119 - 20119-20120 - 20120-20121 - 20121-20122 - 20122-20123

20123-20124 - 20124-20125 - 20125-20126 - 20126-20127 - 20127-20128 - 20128-20129

20129-20130 - 20130-20131 - 20131-20132 - 20132-20133 - 20133-20134 - 20134-20135

20135-20136 - 20136-20137 - 20137-20138 - 20138-20139 - 20139-20140 - 20140-20141

20141-20142 - 20142-20143 - 20143-20144 - 20144-20145 - 20145-20146 - 20146-20147

20147-20148 - 20148-20149 - 20149-20150 - 20150-20151 - 20151-20152 - 20152-20153

20153-20154 - 20154-20155 - 20155-20156 - 20156-20157 - 20157-20158 - 20158-20159

20159-20160 - 20160-20161 - 20161-20162 - 20162-20163 - 20163-20164 - 20164-20165

20165-20166 - 20166-20167 - 20167-20168 - 20168-20169 - 20169-20170 - 20170-20171

20171-20172 - 20172-20173 - 20173-20174 - 20174-20175 - 20175-20176 - 20176-20177

20177-20178 - 20178-20179 - 20179-20180 - 20180-20181 - 20181-20182 - 20182-20183

20183-20184 - 20184-20185 - 20185-20186 - 20186-20187 - 20187-20188 - 20188-20189

20189-20190 - 20190-20191 - 20191-20192 - 20192-20193 - 20193-20194 - 20194-20195

20195-20196 - 20196-20197 - 20197-20198 - 20198-20199 - 20199-20200 - 20200-20201

20201-20202 - 20202-20203 - 20203-20204 - 20204-20205 - 20205-20206 - 20206-20207

20207-20208 - 20208-20209 - 20209-20210 - 20210-20211 - 20211-20212 - 20212-20213

20213-20214 - 20214-20215 - 20215-20216 - 20216-20217 - 20217-20218 - 20218-20219

20219-20220 - 20220-20221 - 20221-20222 - 20222-20223 - 20223-20224 - 20224-20225

20225-20226 - 20226-20227 - 20227-20228 - 20228-20229 - 20229-20230 - 20230-20231

20231-20232 - 20232-20233 - 20233-20234 - 20234-20235 - 20235-20236 - 20236-20237

20237-20238 - 20238-20239 - 20239-20240 - 20240-20241 - 20241-20242 - 20242-20243

20243-20244 - 20244-20245 - 20245-20246 - 20246-20247 - 20247-20248 - 20248-20249

20249-20250 - 20250-20251 - 20251-20252 - 20252-20253 - 20253-20254 - 20254-20255

20255-20256 - 20256-20257 - 20257-20258 - 20258-20259 - 20259-20260 - 20260-20261

20261-20262 - 20262-20263 - 20263-20264 - 20264-20265 - 20265-20266 - 20266-20267

20267-20268 - 20268-20269 - 20269-20270 - 20270-20271 - 20271-20272 - 20272-20273

20273-20274 - 20274-20275 - 20275-20276 - 20276-20277 - 20277-20278 - 20278-20279

20279-20280 - 20280-20281 - 20281-20282 - 20282-20283 - 20283-20284 - 20284-20285

20285-20286 - 20286-20287 - 20287-20288 - 20288-20289 - 20289-20290 - 20290-20291

20291-20292 - 20292-20293 - 20293-20294 - 20294-20295 - 20295-20296 - 20296-20297

20297-20298 - 20298-20299 - 20299-20300 - 20300-20301 - 20301-20302 - 20302-20303

20303-20304 - 20304-20305 - 20305-20306 - 20306-20307 - 20307-20308 - 20308-20309

20309-20310 - 20310-20311 - 20311-20312 - 20312-20313 - 20313-20314 - 20314-20315

20315-20316 - 20316-20317 - 20317-20318 - 20318-20319 - 20319-20320 - 20320-20321

20321-20322 - 20322-20323 - 20323-20324 - 20324-20325 - 20325-20326 - 20326-20327

20327-20328 - 20328-20329 - 20329-20330 - 20330-20331 - 20331-20332 - 20332-20333

20333-20334 - 20334-20335 - 20335-20336 - 20336-20337 - 20337-20338 - 20338-20339

20339-20340 - 20340-20341 - 20341-20342 - 20342-20343 - 20343-20344 - 20344-20345

20345-20346 - 20346-20347 - 20347-20348 - 20348-20349 - 20349-20350 - 20350-20351

20351-20352 - 20352-20353 - 20353-20354 - 20354-20355 - 20355-20356 - 20356-20357

20357-20358 - 20358-20359 - 20359-20360 - 20360-20361 - 20361-20362 - 20362-20363

20363-20364 - 20364-20365 - 20365-20366 - 20366-20367 - 20367-20368 - 20368-20369

20369-20370 - 20370-20371 - 20371-20372 - 20372-20373 - 20373-20374 - 20374-20375

20375-20376 - 20376-20377 - 20377-20378 - 20378-20379 - 20379-20380 - 20380-20381

20381-20382 - 20382-20383 - 20383-20384 - 20384-20385 - 20385-20386 - 20386-20387

20387-20388 - 20388-20389 - 20389-20390 - 20390-20391 - 20391-20392 - 20392-20393

20393-20394 - 20394-20395 - 20395-20396 - 20396-20397 - 20397-20398 - 20398-20399

20399-20400 - 20400-20401 - 20401-20402 - 20402-20403 - 20403-20404 - 20404-20405

20405-20406 - 20406-20407 - 20407-20408 - 20408-20409 - 20409-20410 - 20410-20411

20411-20412 - 20412-20413 - 20413-20414 - 20414-20415 - 20415-20416 - 20416-20417

20417-20418 - 20418-20419 - 20419-20420 - 20420-20421 - 20421-20422 - 20422-20423

20423-20424 - 20424-20425 - 20425-20426 - 20426-20427 - 20427-20428 - 20428-20429

20429-20430 - 20430-20431 - 20431-20432 - 20432-20433 - 20433-20434 - 20434-20435

20435-20436 - 20436-20437 - 20437-20438 - 20438-20439 - 20439-20440 - 20440-20441

20441-20442 - 20442-20443 - 20443-20444 - 20444-20445 - 20445-20446 - 20446-20447

20447-20448 - 20448-20449 - 20449-20450 - 20450-20451 - 20451-20452 - 20452-20453

20453-20454 - 20454-20455 - 20455-20456 - 20456-20457 - 20457-20458 - 20458-20459

20459-20460 - 20460-20461 - 20461-20462 - 20462-20463 - 20463-20464 - 20464-20465

20465-20466 - 20466-20467 - 20467-20468 - 20468-20469 - 20469-20470 - 20470-20471

20471-20472 - 20472-20473 - 20473-20474 - 20474-20475 - 20475-20476 - 20476-20477

20477-20478 - 20478-20479 - 20479-20480 - 20480-20481 - 20481-20482 - 20482-20483

20483-20484 - 20484-20485 - 20485-20486 - 20486-20487 - 20487-20488 - 20488-20489

20489-20490 - 20490-20491 - 20491-20492 - 20492-20493 - 20493-20494 - 20494-20495

20495-20496 - 20496-20497 - 20497-20498 - 20498-20499 - 20499-20500 - 20500-20501

20501-20502 - 20502-20503 - 20503-20504 - 20504-20505 - 20505-20506 - 20506-20507

20507-20508 - 20508-20509 - 20509-20510 - 20510-20511 - 20511-20512 - 20512-20513

20513-20514 - 20514-20515 - 20515-20516 - 20516-20517 - 20517-20518 - 20518-20519

20519-20520 - 20520-20521 - 20521-20522 - 20522-20523 - 20523-20524 - 20524-20525

20525-20526 - 20526-20527 - 20527-20528 - 20528-20529 - 20529-20530 - 20530-20531

20531-20532 - 20532-20533 - 20533-20534 - 20534-20535 - 20535-20536 - 20536-20537

20537-20538 - 20538-20539 - 20539-20540 - 20540-20541 - 20541-20542 - 20542-20543

20543-20544 - 20544-20545 - 20545-20546 - 20546-20547 - 20547-20548 - 20548-20549

20549-20550 - 20550-20551 - 20551-20552 - 20552-20553 - 20553-20554 - 20554-20555

20555-20556 - 20556-20557 - 20557-20558 - 20558-20559 - 20559-20560 - 20560-20561

20561-20562 - 20562-20563 - 20563-20564 - 20564-20565 - 20565-20566 - 20566-20567

20567-20568 - 20568-20569 - 20569-20570 - 20570-20571 - 20571-20572 - 20572-20573

20573-20574 - 20574-20575 - 20575-20576 - 20576-20577 - 20577-20578 - 20578-20579

20579-20580 - 20580-20581 - 20581-20582 - 20582-20583 - 20583-20584 - 20584-20585

20585-20586 - 20586-20587 - 20587-20588 - 20588-20589 - 20589-20590 - 20590-20591

20591-20592 - 20592-20593 - 20593-20594 - 20594-20595

Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation



Patentamt
European Office

des brevets
European

Office européen
europäisches

Amendment No:	01200831.4	Applicant no.:	Demande n°:
Amended:	05/03/01	Date of filing:	Date de dépôt:
Applicant(s):	ALKZO NODER N.V.	Demandeur(s):	6824 BM Arnhem
Amended by:	NETHERLANDS	Title of the invention:	Beschreibung der Erfindung:
Doped antifouling clay's			

Titre de l'invention:
Title of the invention:
Beschreibung der Erfindung:

Doped antifouling clay's

State:	US	Date:	09/02/01	Priority(ies) claimed / Priorité(s) revendiquée(s)
State:	USA	Date:	AKtenzeichen:	103681
Priority(ies) claimed / Priorité(s) revendiquée(s)		File no.:		Numéro de dépôt:
				Payés:

Internationale Patentklassifikation:
International Patent classification:
Classification internationale des brevets:

Am Anmeldetag benannte Vertragsstaaten:
Contracting states designated at date of filing: AT/BE/CH/CY/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE/TR
Bemerkungen:
Remarks:

Remarques:
Bemerkungen:

1. Introduction of TUG and TUG's contribution

1. The first stage of the process is the **initialization**. This stage involves setting up the initial state of the system, which includes defining the initial values for all variables and parameters.

30 F. Cavaani et al "Hydroxalite-type anionic clays: Preparation, Properties and Applications," *Catalysis Today*, 11 (1991) Elsevier Science Publishers B.V.

25 The preparation of anionic clays has been described in many prior art publications. Two major reviews of anionic clay chemistry were published in which the synthesis methods available for anionic clay synthesis have been summarized:

20 It should be noted that a variety of terms are used to describe the material that is referred to in this specification as an anionic clay. Hydroxalite-like and layered double hydroxide are referred to these materials as anionic clays, comprising within this specification we refer to those skilled in the art. In that term hydroxalite-like and layered double hydroxide materials.

15 In hydroxalite-like anionic clays the brucite-like main layers are built up of octahedra alternating with interlayers in which water molecules and anions, more particularly carbonate ions, are distributed. The interlayers may contain anions such as NO_3^- , OH^- , Cl^- , Br^- , I^- , SO_4^{2-} , SiO_4^{2-} , CrO_4^{2-} , BO_3^{2-} , MnO_4^- , GaO_4^- , VO_4^{2-} , ClO_4^- , BO_3^{2-} , pillarizing anions such as $\text{V}_{10}\text{O}_{28}^{6-}$ and $\text{Mo}_{10}\text{O}_{24}^{6-}$, monocarboxylates such as acetate, dicarboxylates such as oxalate, alkyl sulphonates such as laurylsulphonate.

10 Anionic clays have a crystal structure which consists of positively charged layers built up of specific combinations of metal hydroxides between which there are anions and water molecules. Hydroxalite is an example of a naturally occurring anionic clay, in which carbonate is the predominant anion present. Melixenite is an anionic clay wherein hydroxyl is the predominant anion present. 5 And doped anionic clays prepared by said process.

This invention relates to a process for the preparation of doped anionic clays,

05 03 2001 ACH 2853 PDEP

DOPED ANIONIC CLAYS

44

- In addition there is an extensive amount of patent literature on the use of
 15 for work on anionic clays, reference is further made to the following articles:
 20 metal salts. The second method is the salt-oxide method in which a divalent metal
 oxide is reacted at atmospheric pressure with a soluble trivalent metal
 size. The second method is the salt-oxide method in which a divalent metal
 optionally followed by hydrothermal treatment or aging to increase the crystallite
 conventional method is co-precipitation (in: Besse this method is called the salt-
 25 base method) of a soluble divalent metal salt and a soluble trivalent metal
 size. The second method is the salt-oxide method in which a divalent metal
 followed by aging under atmospheric pressure. This method has only been
 described for the use of ZnO and CuO in combination with soluble trivalent
 30 metal salts. Clay Chemistry and Physics, 14, 569 (1986).
 Clays and Clay Minerals, 28, 50 (1980).
 Clays and Clay Minerals, 23, 369 (1975).
 Chemistry Letters (Japan), 843 (1973).

Two types of anionic clay preparation are described in these reviews. The most
 15 conventional method is co-precipitation (in: Besse this method is called the salt-
 base method) of a soluble divalent metal salt and a soluble trivalent metal salt,
 conventionally followed by hydrothermal treatment or aging to increase the crystallite
 size. The second method is the salt-oxide method in which a divalent metal
 20 size. The second method is the salt-oxide method in which a divalent metal
 oxide is reacted at atmospheric pressure with a soluble trivalent metal
 size. The second method is the salt-oxide method in which a divalent metal
 optionally followed by hydrothermal treatment or aging to increase the crystallite
 conventional method is co-precipitation (in: Besse this method is called the salt-
 25 base method) of a soluble divalent metal salt and a soluble trivalent metal
 size. The second method is the salt-oxide method in which a divalent metal
 followed by aging under atmospheric pressure. This method has only been
 described for the use of ZnO and CuO in combination with soluble trivalent
 30 metal salts. Clay Chemistry and Physics, 14, 569 (1986).
 Clays and Clay Minerals, 28, 50 (1980).
 Clays and Clay Minerals, 23, 369 (1975).
 Chemistry Letters (Japan), 843 (1973).

J P Besse and others "Anionic clays: trends in pillaray chemistry, its synthesis
 and microporous solids" (1992), 2, 108, editors: M.L. Ocelli, H.E. Robson, Van
 Nostrand Reinhold, N.Y.
 Amsterdam.

There are many applications of anionic clays. These include but are not restricted to: catalysts, adsorbents, drilling muds, catalyst supports and carriers, extenders and applications in the medical field. In particular Van Broekhoven 30

using aluminum trihydrate as aluminum source, anionic clays are not formed. Comparative Examples 1-3 presented in all these patents indicate that upon 25 5,728,365, US 5,728,366, US 5,730,951, US 5,776,424, US 5,578,286. The wise manner and under non-hydrothermal conditions: US 5,728,364 US i.e. anionic clays, but of magnesium oxide and a transition alumina, in a batch- Several patents in the name of Alcoa describe the synthesis of hydrotalcites, 30

trihydrate or a thermally treated form thereof. WO 99/41197 discloses the production of an anionic clay-containing composition comprising a Mg-Al anionic clay and unreacted aluminum 20

WO 99/41195 a continuous process is described for the production of a Mg-Al anionic clay from a Mg source and aluminum trihydrate:

WO 99/41196 discloses the preparation of anionic clays with acetate as the charge balancing anion from magnesium acetate, another magnesium source and aluminum trihydrate.

WO 99/41198 relates to the production of anionic clay from two types of aluminum compounds and a magnesium source. One of the aluminum sources is aluminum trihydrate or a thermally treated form thereof.

Recently, patent applications relating to the production of anionic clays from inexpensive raw materials have been published. These materials include magnesium oxide and aluminum trihydrate.

anionic clays and processes for their preparation.

(US 4,956,581 and US 4,952,382) has described their use in SO_x abatement for several applications the presence of additives, both metals and non-metals, within the anionic clay is desirable. These additives are used to alter or enhance certain properties of the anionic clay. For instance, Ce and V are added to the anionic clay to obtain material suitable for SO_x removal in FCC. In general, these additives are deposited on the anionic clay by impregnation. With impregnation, however, it is often difficult to obtain a homogeneous dispersion of the additive within the anionic clay or, if it is difficult to deposit enough additive on the anionic clay to obtain the desired properties.

Some patent publications indicate that the additives may be added to the reaction mixture during preparation of the anionic clay. However, when additives are added to the reaction mixture, their presence may interfere with precipitation. It is possible that the pH required to precipitate for example the anionic clay formation. For instance, when anionic clays are made by co-additives are added to the reaction mixture, their presence may interfere with precipitation. In extreme situations the additive may be precipitated in advance of the magnesium and aluminum sources or may not be sufficiently precipitated.

This invention relates to a process for preparing doped anionic clays, wherein the dopant is already incorporated in the starting material. With this process (hereinafter referred to as dopant). Further, the process allows additive anionic clay can be prepared containing controlled amounts of additive the dopant is dispersed within the anionic clay. The invention pertains to the preparation of doped magnesium source, i.e. doped brucite or doped MgO, to obtain a doped source, at least one of the metal sources being either doped boehmite or a anionic clay wherein a trivalent metal source is reacted with a divalent metal dispersing of the dopant within the anionic clay.

The process according to the invention pertains to the preparation of doped anionic clay which is a trivalent metal source is reacted with a divalent metal anionic clay. The invention also relates to the dispersion of the dopant within the anionic clay. The invention further relates to the dispersion of the dopant within the anionic clay. The invention further relates to the dispersion of the dopant within the anionic clay.

anionic clay.

05-03-2001

Mo, W, V, Sn), actinides, rare earth metals such as La, Ce, Nd, noble metals Ba), alkaline metals, transition metals (for example Mn, Fe, Ti, Zr, Cu, Ni, Zn, elements selected from the group of alkaline earth metals (for instance Ca and homogeneous dispersed state. Suitable additives are compounds containing and an additive are converted to a boehmite containing the additive in a invention can be prepared in several ways. In general, a boehmite precursor 25 doped anionic clay. The doped boehmite used in the process according to the boehmite and/or a doped magnesium source is used as starting material for the As mentioned above, in the process according to the invention a doped 30

Doped boehmite

20

and/or spinel. The invention also relates to a process according to which a doped boehmite is obtained by heating a doped anionic clay at a temperature between 300° and 1200°C to form a doped solid solution at a temperature between 300° and 1200°C to form a doped solid solution 15 anionic clay prepared by the process according to the invention, is heat-treated Therefore, the present invention is also directed to a process wherein a doped

15

adsorbent is converted from an anionic clay into a solid solution. Thus in the solid solution form. During use in a FCC unit, the catalyst or anionic clay according to the invention is usually heated during preparation and SO_x adsorbent for cracking reactions), or a catalyst support, the 10 temperatures spindles. When used as a catalyst, an adsorbent (for instance a Upon being heated anionic clays generally form solid solutions, and at higher temperatures does not interfere with the formation of the anionic clay.

10

and/or boehmite does not interfere with the formation of the anionic clay. It was found further that the dopant present either in the magnesium source 5 homogeneous and enough additive can be deposited on the anionic clay. It anionic clay can be controlled easily, i.e. the dopant can be dispersed and/or doped magnesium source, the amount of dopant ending up in the It was found that when using a doped starting material such as doped boehmite

5

30 The boehmite can also be prepared by aging an aqueous slurry containing a thermally treated form of aluminum trihydrate and additive(s) at temperatures

Process 3

25 added while the hydrolysis and precipitation are going on or at the end in the aging step. The boehmite can be prepared by hydrolysis and precipitation as hydroxides of suitable aluminum salts and aged to form a doped boehmite. Examples of chloride, sodium aluminate, and mixtures thereof. The additive(s) may be soluble aluminum salts and aged to form a doped boehmite. Examples of

20

Process 2

15 can be incorporated during the hydrolysis step or added at the end before the aging step. The boehmite can be prepared by hydrolyzing and aging an aluminum alkoxide in the presence of a compound containing the desired additive(s). The additive can be incorporated during the hydrolysis step or added at the end before the

Process 1

10 Examples of suitable preparation processes for the doped boehmites are described below:

5 Suitable compounds containing the desired elements are nitrates, sulfates, chlorides, formates, acetates, oxalates, alkoxides, carbonates, vanadates, etcetera. The use of compounds with heat-decomposable anions is preferred, because the resulting boehmites with additive can be dried directly, without any washing, as anions undesirable for catalytic purposes are not present.

such as Pt and Pd, silicon, gallium, boron, titanium, and phosphorus.

The doped boehmite can also be prepared by aging an aqueous slurry containing amorphous alumina gel and additive(s) at temperatures ranging from 60° to 250°C, preferably at a temperature between 80° and 150°C, to form boehmites. Like process 3 mentioned above, this preparation method also has the advantage that no ions are introduced into the boehmite apart from the ions of the additive compound. This means that with the appropriate choice of additive compounds washing steps can be reduced or avoided altogether.

Process 4

undesirable for catalytic purposes are not present.

ACH 2853 PDEP

By using a combination of doped boehmite and non-doped aluminum sources the above-mentioned trivalent metal sources can be used.

30 carbonates, nitrates, chlorides, chlorohydrates, and alkoxides. Also mixtures of manganese sources are the respective oxides, hydroxides, oxalates, cobalt, manganese. Suitable gallium, indium, iron, chromium, vanadium, cobalt, aluminate, as well as sources of gallium, indium, iron, chromium, vanadium, aluminum nitrate, aluminum chloride, aluminum chlorohydrate and sodium flash calcined aluminia, gels, non-doped boehmite) aluminum salts such as aqueous suspension such as oxides and hydroxides of aluminum, (e.g. soils, metal sources beside (or other than) doped boehmite may be added to the slurry. As mentioned above, in the process according to our invention trivalent boehmite is added to the reactor in the form of an aqueous suspension or another trivalent metal source can also be used. Preferably the doped combinations of doped boehmites or combinations of doped boehmite and

the seed) are introduced into the boehmite.

15 ions other than the ions of the additive (and the optional additives present in described above can suitably be used as a seed. Like processes 3, 4, and 5 no doped with additives. Also boehmites prepared by one of the processes sodium aluminate solutions, etcetera. Additionally, the seeds may have been etcetera), amorphous seeds, milled boehmite seeds, boehmite prepared from commercially available boehmite (Catapal®, Condea® P3®, Versal, P-200®, suitable seeds are the known seeds to make microcrystalline boehmite such as boehmite seeds in the presence of compounds of the desired additives. gibbsite, BOC, and bayerrite by hydrothermal treatment, with the aid of suitable Doped Boehmites can also be prepared by aging aluminum trihydrates such as

5

Process 6

No ions other than the ions of the additive compound are introduced into the boehmite with this process.

the aqueous suspension such as metal sources of zinc, nickel, copper, iron, cobalt, manganese, calcium, barium. Suitable zinc, nickel, copper, iron, cobalt, the aqueous suspension such as metal sources of zinc, nickel, copper, iron, sources beside (or other than) the doped magnesium source may be added to mentioned above, in the process according to our invention divalent metal added to the reactor in the form of an aqueous suspension or slurry. As metal source can also be used. Preferably the doped magnesium source is mentioned above, in the process according to our invention divalent metal sources or combinations of a doped magnesium source and another divalent clays such as dolomite, sepiolite, magnesite. Combinations of doped magnesium bicarbonate, magnesium nitrate, magnesium chloride, magnesium-carbonating acetate, magnesium carbonate, magnesium hydroxy carbonate, magnesium salts such as magnesium acetate, magnesium formate, magnesium hydroxy state.

20 Suitable brucite or MgO precursors are $Mg(OH)_2$, hydromagnesite, magnesium

be prepared, with the dopants being present in a homogeneous dispersed to obtain the doped magnesium source. In this way doped brucite or MgO can precursor thereof in an aqueous suspension and thermally treating said mixture by adding an additive such as the ones described-above to brucite, MgO or a 15 Doped magnesium source, i.e., doped brucite or doped MgO, can be prepared

Doped magnesium source

improves the nickel encapsulation-capacity of the anionic clay. For instance, alumina provides acid sites for catalytic cracking and boehmite provide different types of desirable functionalities for the anionic clay. For alumina improves the binding properties of the anionic clay and may also to convert all of the trivalent metal source into doped anionic clay. Excess combinations thereof, all optionally in the presence of seeds. It is not necessary treatment with acid or base, thermal and/or hydrothermal treatment, or to the addition to the reaction mixture. Said pre-treatment may involve The doped boehmite and other trivalent metal sources may be pre-treated prior the amount of dopant present in the final anionic clay can be controlled.

5

10

The doped starting material(s) and optionally additional divalent and/or trivalent metal sources are added to a reactor and heat-treated in aqueous suspension to obtain a doped anionic clay. Within the context of this invention a reactor is

Conditions

25 compounds can be same or different.

In the embodiment in which both doped boehmite and doped magnesium source are used in the process, the additive (dopant) in these doped

Doped boehmite and doped magnesium source

20 acid streams of gases or liquids.

It is not necessary to convert all of the divalent metal source into doped anionic sites which render the anionic clay suitable for removing or neutralising strong sites for instance metal trap capacity. The presence of magnesia provides basic alumina-magnesia in the anionic clay may provide desirable functionalities such as for instance, metal trap capacity. The presence of magnesia or magnesium will be referred to in the description as magnesia. The presence of magnesia or brucite, magnesia or alumina-magnesia, doped or not, as the case may be. For another magnesium source will usually be present in the final product as clay. For instance, any excess magnesium, either doped brucite, doped MgO or clay. By using of a combination of doped magnesium source and non-doped magnesium source the amount of dopant in the anionic clay can be controlled.

5 therefore, optionally in the presence of seeds.

sources can be used. The divalent metal source may be pre-treated prior to the addition to the reaction mixture. Said pre-treatment may comprise a thermal nitrates, chlorides. Also mixtures of the above-mentioned divalent metal nitrates, manganese, calcium, barium sources are oxides, hydroxides, carbonates,

30 deleterious cations remain in the anionic clay.

Preferred pH modifier is an ammonium base, because upon drying no trivalent metal source before they are fed to the reactor. An example of a pH, may be fed to the reactor or added to either the divalent metal source or if desired, organic or inorganic acids and bases, for example for control of the

25

mixture.

The final anionic clay may conveniently be obtained by drying the resulting

20 may also be conducted partly batch-wise and partly continuously. The process continuous mode, optionally in a continuous multi-step operation. The process

The process according to the invention may be conducted batch-wise or in a

slurry or solution, either to the reactor or the doped Boehmite slurry.

15 either the divalent metal source per se, or add the divalent metal source in a instance the doped Boehmite slurry at elevated temperature and then add versa and adding the resulting slurry to the reactor. It is possible to treat, for adding the divalent metal source to a slurry of trivalent metal source or vice slurries of the starting materials, either combined or separate, to the reactor or Said aqueous suspension in the reactor may be obtained by either adding

10

etcetera.

5 infrared sources, heating jackets (either electrical or with a heating fluid), lamps, reactor may be heated by any heating source such as a furnace, microwave, (up to 400 °C) at increased pressure, i.e. under hydrothermal conditions. The

between 50° and 100°C at atmospheric pressure and at higher temperatures

The reaction can take place with or without stirring and at temperatures

with stirrers, baffles, etcetera to ensure homogeneous mixing of the reactants.

metal source and divalent source takes place. The reactor may be equipped

considered to be any confined zone in which the reaction between the trivalent

5

The product formed may optionally be calcined at temperatures between 300° and 1200°C, preferably between 300° and 800°C and most preferred between 300° and 600°C. This calcination is conducted for 15 minutes to 24 hours, preferably 1-12 hours and most preferred 2-6 hours. By this treatment the anionic clay will be transformed into a solid solution and/or spinel. Solid solutions possess the well known memory effect, which means that they can be transformed back into anionic clays upon rehydration. This rehydration can be performed by contacting the solid solution with water for 1-24 hours at 65°-85°C. Preferably, the slurry is stirred and has a solids content ranging from about 10 to 50 wt%. During this treatment additives can be added.

If desired, the doped anionic clay prepared by the process according to the invention may be subjected to ion-exchange. Upon ion-exchange the interlayer exchange-balancing anions are replaced with other anions. Said other anions are the ones commonly present in anionic clays and include pillaring anions such as VO_4^{2-} , HVO_4^{2-} , VO_3^{3-} , $\text{V}_2\text{O}_5^{6-}$, $\text{Mo}_7\text{O}_{24}^{6-}$, $\text{PW}_{12}\text{O}_{40}^{3-}$, $\text{B}(\text{OH})_4^-$, $[\text{B}_3\text{O}_3(\text{OH})_6]^{2-}$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, HBO_2^- , HGAO_3^- , CrO_4^{2-} , Keggin-ions, formates, acetate, and mixtures thereof. Examples of suitable pillaring anions are given in US 4,774,212 which is included by reference for this purpose. Said ion-exchange can be conducted before or after drying the anionic clay-containing composition formed in the slurry.

The process of the invention provides wide flexibility in preparing products with a wide range of divalent to trivalent metal molar ratios. This ratio can vary from 0.1 to 10, preferably from 1 to 6, more preferred from 2 to 4, and especially 0.1 to 10, preferably from 1 to 6, more preferred from 2 to 4, and especially 30 additional additives, both metal compounds and non-metal compounds, such as rare earth metals, Si, P, B, group VI, group VII, alkaline earth (for instance the doped boehmite or doped magnesium source, it may be desirable to add in addition to the additives already incorporated into the anionic clay by using

30 bodies

The resulting doped anionic clays may optionally be shaped to form shaped bodies. If composites containing doped anionic clay and (doped) boehmite are formed, this boehmite can serve as a binder and create porosity in the shaped

metal compound and/or trivalent metal compound. These compositions appear to be highly suitable for use as an additive or as a matrix for catalysts for hydrocarbon conversion. Moreover, these compositions appear especially suitable for sulfur removal from the gasoline and diesel fraction in FCC, SO_x and NO_x removal in FCC, and as a metal trap.

the invention by controlling the process conditions; In said compositions the doped anionic clay, divalent metal compound, and/or triivalent metal compound are intimately mixed, rather than present as separate phases such as in physically mixed mixtures of doped anionic clay, divalent

On the other hand, divalent metal sources may be used in excess to obtain a composition containing doped anionic clay and a divalent metal compound, usually in the form of an oxide or hydroxide. It is even possible to prepare compositions containing anionic clay, trivalent metal compound and a divalent metal compound with the process according to M15

If an excess of trivalent compound is used a composition is obtained which contains doped anionic clay and also trivalent metal compound usually in the

Ca and Ba) and/or transition metals (for example Mn, Fe, Ti, Zr, Cu, Ni, Zn, Mo, Sn, V, W), to the anionic clay. Said additives can be deposited on the doped anionic clay according to the invention or they can be added either to the divalent metal source or the trivalent metal source which are added to the reactor or added to the reactor separately. Suitable sources of metal compounds or non-metal compounds are oxides, halides or any other salt such as chlorides, nitrates etcetera.

The doped anionic clay-containing bodies may also be prepared to contain conventional catalyst components such as kaolin, titaniium oxide, zirconia, alumina, silica, silica-aluminia, bentonite etcetera), molecular sieve material (e.g. zeolite Y USY zeolite, ion-exchanged zeolite, ZSM-5, beta-zeolite, ST-5 etcetera). Typically, such conventional catalyst components or precursors thereof may be added prior to the shaping step.

Suitable shaping methods include spray-drying, pelletising, extrusion (optionally combined with kneading), beadling, or any other conventional shaping method used in the catalyst and absorbent fields or combinations thereof. The amount of liquid present in the slurry used for shaping should be adapted to the specific shaping step to be conducted. It might be advisable to partially remove the liquid used in the slurry and/or add an additional or another liquid, and/or change the pH of the precursor mixture to make the slurry gelable and thus suitable for shaping. Various additives commonly used in the various shaping methods such as extrusion additives may be added to the precursor mixture used for shaping.

20 The doped anionic clay can suitably be used as a component of a catalyst composition.

The present invention is illustrated by the following examples.

EXAMPLES**Example 1**

5 A suspension of Condea P-3® alumina in a $Zn(NO_3)_2$ solution was homogenised by high shear mixing for 15 minutes. The mixture was aged at 85°C for 24 hours. This resulted in a Zn^{2+} -doped boehmite containing around 10 wt% ZnO.

8 A suspension of Condea P-3® alumina in a $Zn(NO_3)_2$ solution was homogenised by high shear mixing for 15 minutes. The mixture was aged at 85°C for 24 hours. This resulted in a Zn^{2+} -doped boehmite containing around 10 wt% ZnO.

10 To the doped boehmite-containing slurry a MgO-containing slurry with a pH of 7.42 and a temperature of 44°C was added in an amount sufficient to obtain a Mg/Al molar ratio of 2.3. Subsequently, the mixture was aged at 85°C for 24 hours. The slurry had a solids content of approximately 25 wt% and a pH of 8.92. The final product was dried at 100°C. Powder X-ray diffraction (PXRD) indicated the formation of anionic clay.

15 A suspension of Condea P-3® alumina in a $Zn(NO_3)_2$ solution was homogenised by high shear mixing for 15 minutes. The mixture was aged at 85°C for 24 hours. This resulted in a Zn^{2+} -doped boehmite containing around 10 wt% ZnO. To the doped boehmite-containing slurry a MgO-containing slurry with a pH of 7.42 and a temperature of 44°C was added in an amount sufficient to obtain a Mg/Al molar ratio of 2.3. Subsequently, the mixture was aged at 165°C and autogenous pressure for 2 hours. The slurry had a solids content of 25 wt% and a pH of 7.42 and a temperature of 44°C was added in an amount sufficient to obtain a Mg/Al molar ratio of 2.3. Subsequently, the mixture was aged hydrothermally at 165°C and autogenous pressure for 2 hours. The slurry had a solids content of approximately 25 wt% and a pH of 8.92. The final product was dried at 100°C. PXRD indicated the formation of anionic clay.

Example 3

30

Example 4

To the doped boehmite-containing slurry a MgO-containing slurry with a pH of 7.42 and a temperature of 44°C was added in an amount sufficient to obtain a Mg/Al molar ratio of 2.3. Following addition of NaOH/Na₂CO₃ (1M final concentration), the mixture was aged at 85°C for 24 hours. The initial pH of the slurry was 10. The product was filtered, washed with water and dried at 100°C. PXRD indicated the formation of anionic clay.

homogenised by high shear mixing for 15 minutes. The mixture was aged at 85°C for 24 hours. This resulted in a Zn²⁺-doped boehmite containing around 10 wt% ZnO.

To the doped boehmite-containing slurry a MgO-containing slurry with a pH of 7.42 and a temperature of 44°C was added in an amount sufficient to obtain a Mg/Al molar ratio of 2.3. Following addition of NaOH/Na₂CO₃ (1M final concentration), the initial pH of the slurry was 10. The product was filtered, washed with water and dried at 100°C. PXRD indicated the formation of anionic clay.

Example 5

CeO₂-doped boehmite was prepared by suspending Condea F-3® alumina in a (NH₄)₂Ce(NO₃)₆ solution with a pH of 7.42 and a temperature of 44°C with high shear mixing for 15 minutes. The suspension was treated at 85°C for 24 hours. The product was not dried. The resulting doped boehmite containing around 10 wt% CeO₂.

MgO was added to the slurry. The resulting slurry had a pH of 8.92, a solids content of about 25 wt% and a temperature of 52°C. The Mg/Al ratio in the resulting CeO₂-doped boehmite containing around 10 wt% CeO₂.

slurry was 2.3. The slurry was aged at 85°C for 24 hours. The product was dried overnight at 100°C. PXRD indicated the formation of anionic clay.

ACH 2853 PDEP

17

Example 6

5

CeO₂-doped boehmite was prepared by suspending Condea P-3® alumina in a (NH₄)₂Ce(NO₃)₆ solution with a pH of 7.42 and a temperature of 44°C with high shear mixing for 15 minutes. The suspension was aged at 85°C for 24 hours. The product was not dried. The resulting doped boehmite containing around 10 wt% CeO₂.

10

MgO was added to the slurry. The resulting slurry had a pH of 8.92, a solids content of about 25 wt% and a temperature of 52°C. The Mg/Al ratio in the slurry was 2.3. The slurry was aged hydrothermally at 165°C at autogenous pressure for 4 hours. The product was dried overnight at 100°C. PXRD indicated the formation of anionic clay.

15

DESC

Printed:08-02-2002

01200831

1. Process for the preparation of doped anionic clay wherein a trivalent metal source is reacted with a divalent metal source, obtain a doped anionic clay.
2. Process according to claim 1, wherein doped boehmite is reacted with a divalent metal source.
3. Process according to claim 1 or 2, wherein doped brucite is reacted with a trivalent metal source.
4. Process according to any one of the claims 1-3, wherein doped MgO is reacted with a trivalent metal source.
5. Process according to any one of the metal sources being either doped boehmite, doped MgO or doped brucite, to obtain a doped anionic clay.
- 10 1. Process for the preparation of doped anionic clay wherein a trivalent metal source is reacted with a divalent metal source.
2. Process according to claim 1, wherein doped boehmite is reacted with a divalent metal source.
3. Process according to claim 1 or 2, wherein doped brucite is reacted with a trivalent metal source.
4. Process according to any one of the claims 1-3, wherein doped MgO is reacted with a trivalent metal source.
- 15 5. Process according to claim 2 wherein in addition to the doped boehmite another trivalent metal source is present in the reaction mixture.
6. Process according to claim 3 wherein in addition to the doped brucite another trivalent metal source is present in the reaction mixture.
- 20 7. Process according to claim 4 wherein in addition to the doped MgO another divalent metal source is present in the reaction mixture.
- 25 8. Process according to any one of claims 1-7 wherein the trivalent metal source and the divalent metal source are reacted under hydrothermal conditions.
9. Process according to any one of claims 1-8 wherein the doped boehmite, the doped MgO and/or the doped brucite contain a rare earth metal.

16. Catalyst additive composition containing doped anionic clay according to claim 13.
15. Catalyst composition containing doped anionic clay according to claim 13.
- 20 14. Shaped body comprising doped anionic clay according to claim 13.
13. Doped anionic clay obtainable the process according to any one of claims 1-10 or 12.
12. Process for the preparation of doped anionic clay, wherein the Mg-Al solid solution obtained by the process of claim 1 is rehydrated to form a doped solution obtainable by the process of claim 11 is subjected to a heat-treatment at a temperature between 300° and 1200°C.
- 10 11. Process for the preparation of a doped Mg-Al solid solution and/or spinel, wherein an anionic clay obtained by any one of the processes according to any one of the previous claims is subjected to a heat-treatment at a temperature between 300° and 1200°C.
- 5 10. Process according to any one of the previous claims, wherein the doped MgO and/or doped brucite obtain a compositions comprising anionic clay and doped boehmite, boehmite, the doped MgO and/or the doped brucite is added in excess to doped MgO and/or doped brucite.
11. Compound.

The present invention is directed to a process for the preparation of a doped anionic clay. In said process a trivalent metal source is reacted with a divalent metal source, at least one of the metal sources being either doped boehmite, doped MgO or doped brucite, to obtain a doped anionic clay.

Suitable dopants are compounds containing elements selected from the group of alkaline earth metals (for instance Ca and Ba), alkaline metals, transition metals (for example Mn, Fe, Ti, Zr, Cu, Ni, Zn, Mo, W, V, Sn), actinides, rare earth metals such as La, Ce, Nd, noble metals such as Pt and Pd, silicon, gallium, boron, titanium, and phosphorus.

10

ABSTRACT

44

